

XEDS and EELS in the TEM at Atmospheric Pressure and High Temperature.

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Recent progress with environmental cell and microscope design has enabled *in situ* imaging studies within gaseous environments inside the (scanning) transmission electron microscope ((S)TEM) to become increasingly routine [1-2]. In contrast, complementary elemental information is more challenging to obtain *in situ*. Electron energy loss spectroscopy (EELS) has been reported inside an environmental TEM [3,4], although only at modest pressure (below ~30 mbar). Closed-cell design specimen holders, in which the specimen and the gaseous environment are sealed from the high vacuum of the TEM by two SiN windows, allow much higher pressures to be reached (up to ~1 bar). However, these environmental cells have two major drawbacks which limit their analytical capabilities: 1) X-ray energy dispersive spectroscopy (XEDS) is challenging, as the walls of the cell generally shadow the detectors, preventing the collection of characteristic X-rays; 2) EELS is challenging as the two 50 nm thick SiN windows cause multiple scattering, which limits signal-to-background ratio in the core-loss EEL spectra and thus significantly degrades performance [5].

Recent improvement in the detection efficiency of both XEDS and EELS allows spectrum images (SIs) to be acquired at high speed and low total electron dose. In this presentation, we demonstrate the improved analytical performance of a closed-cell holder and its application to study alloying and segregation phenomena in PdAg nanoparticles during an *in situ* experiment. We demonstrate that the use of a XEDS compatible Protochips Atmosphere holder in a FEI Titan ChemiSTEM allows elemental mapping to be performed at high spatial resolution, ambient pressure and high temperature using XEDS.

Figure 1 compares XEDS and EELS maps acquired at 820 mbar H₂ and 200°C. The specimen holder was tilted to 25° and only two of the four Super-X XEDS detectors were used. The probe current was set to 600 pA to perform elemental mapping with a pixel time of 20 ms and a pixel size of 5 Å. The EELS “background” relative thickness t/λ is ~ 0.8, due to the two 50 nm thick SiN windows - measured with a 200 kV incident electron beam, 81 mrad EELS collection angle and ~15 μm gas channel height at 1 bar H₂. This makes EELS analysis increasingly problematic for specimens with thicknesses greater than ~50 nm, while XEDS is still effective for much thicker specimens. As the nanoparticles used here have diameters of ~30 nm the Pd and Ag EELS elemental maps in Figure 1 show slightly better signal-to-noise ratio than the corresponding XEDS maps. However, even for these small nanoparticles the background increases significantly on the particles themselves leading to a decrease of the signal-to-background ratio of the Si edge (figure 1 j). Figure 2 shows XEDS maps acquired at 910 mbar 5% O₂/Ar and 350°C. The PdAg nanoparticles change morphology and begin alloying at temperatures above 300°C. To study this it is essential to perform spectrum imaging, as the very similar atomic number of Pd and Ag (46 and 47, respectively) prevents identification using STEM-HAADF imaging alone. Spectroscopic imaging requires higher total electron dose than standard imaging, therefore work is in progress to control beam-induced segregation.

References

- [1] S. Giorgio *et al*, *Ultramicroscopy* **106**, (2006), p. 503
 [2] J. F. Creemer *et al*, *Ultramicroscopy* **108**, (2008), p. 993
 [3] S. Chenna and P. Crozier, *Microsc. Microanal.* **17** (Suppl 2), (2011), p. 476
 [4] P. Crozier and S. Chenna, *Ultramicroscopy* **111**, (2011), p. 177
 [5] N. J. Zaluzec *et al*, *Microsc. Microanal.* **20**, (2014), p. 323
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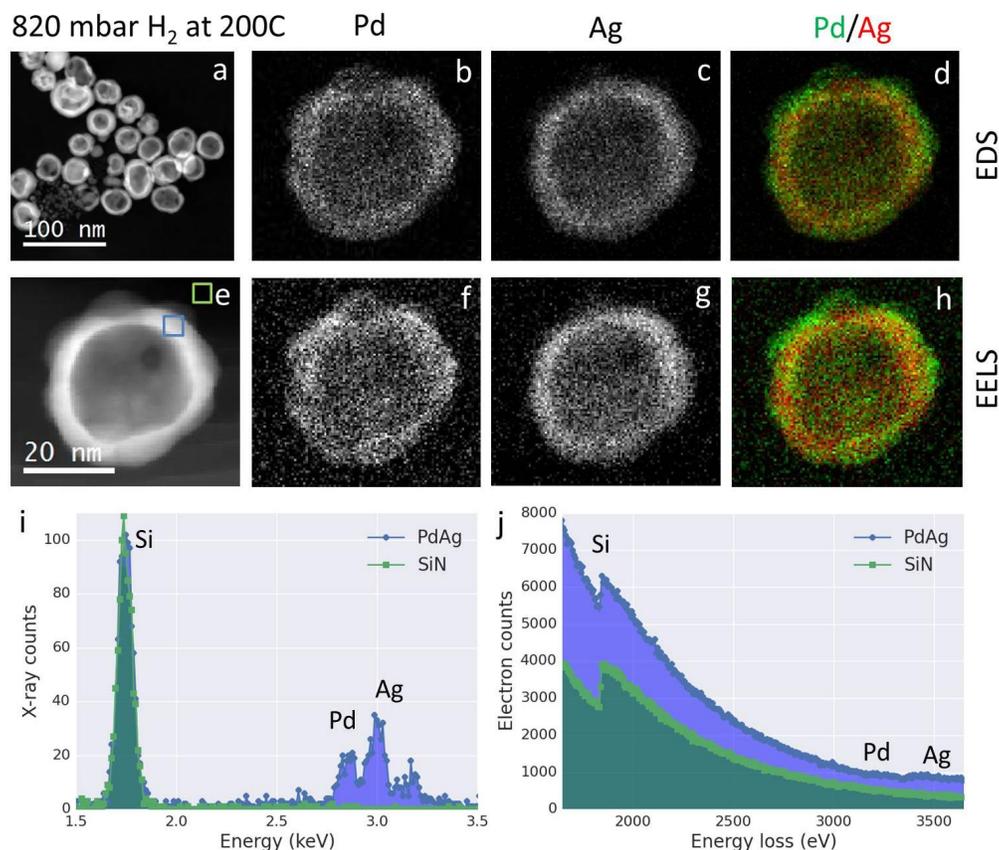


Figure 1. a) Representative STEM-HAADF image showing PdAg nanoparticles in a 820 mbar H₂ at 200°C. b) Pd, c) Ag and d) Pd/Ag composite maps obtained using XEDS. e) STEM-HAADF image acquired simultaneously than the SIs. f) Pd, g) Ag and h) Pd/Ag composite maps obtained using EELS. i) XED and j) EEL spectra of the positions marked in e). All spectra are integrated over 25 pixels.

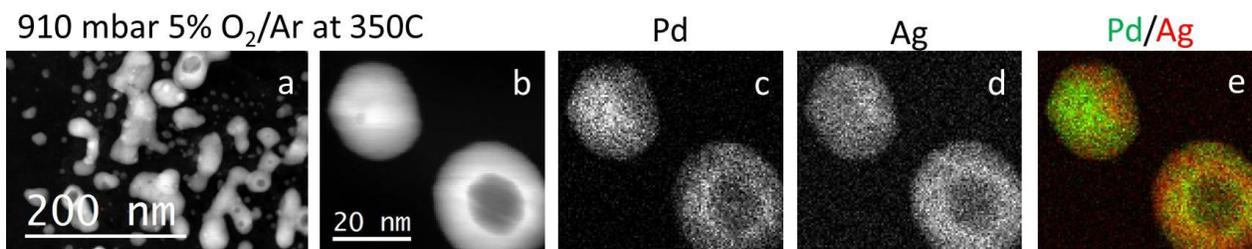


Figure 2. a) Representative STEM-HAADF image of the PdAg nanoparticles at 910 mbar and 350°C b) High-magnification STEM-HAADF image with a 20 nm scale bar. c) Pd, d) Ag and e) Pd/Ag XEDS composite maps.